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DEVELOPMENT
OF
MULTIPURPOSE CAPSULAR ADHESIVE SYSTEMS
FINAL REPORT

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THE NATIONAL CASH REGISTER COMPANY
DAYTON, OHIO

MAY 1971



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PICATINNY ARSENAL

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DEVELOPMENT OF MULTIPURPOSE
CAPSULAR ADHESIVE SYSTEMS

Final Report

By

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May 1971

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ABSTRACT

During the initial phase of this program a unique, polyester-epoxy adhesive system was developed which cures very rapidly upon mixing of its two components and adheres to a multitude of substrates under various environmental conditions.¹ Each of the two liquid adhesive components can be encapsulated to form "pseudo solids". Mixing together of the two capsular components into the proper ratio forms a stable, "one can," dry powder adhesive that is easily activated upon rupture of the capsules.

This rapid curing capsular adhesive system, with its improved stability, handling and logistics characteristics due to encapsulation, was further characterized during the second phase of the program. Capsular adhesive stability was found to be nine months under laboratory conditions with the epoxy component being the limiting factor. Several formulation variations were made that affected cure time, bond strength and adhesion properties. Encapsulation of each of the two components was easily scaled up through the pilot-plant stage. Several mechanical adhesive applicator designs were developed and evaluated for the extrusion and application of both the capsular adhesives and the same formulations in their liquid, unencapsulated forms.

¹ Development of Multipurpose Capsular Adhesive Systems -
Interim Summary Report; Tech. Rpt. 3895, U.S. Army,
Picatinny Arsenal.

ADHESIVE PERFORMANCE SUMMARY

<u>Characteristic</u>	<u>Design Goal (psi)</u>	<u>Actual Values</u>	
		<u>Paste System (psi)</u>	<u>Total-Capsule System (psi)</u>
1. Form bond to submerged substrates in fresh water			
Wood	0.5	44	30
Concrete	0.5	98	150
Steel	100	530	369
Aluminum	100	315	214
Salt Water (steel)	100	453	313
2. Demonstrate a functional bond for 30 days	100	450 (100 days)	255 (100 days)
3. Form bonds over the temperature range from			
52°C	100	96	73
ambient (23°C)	100	530	369
to -4°C	100	375 (10 min. cure)	327 (10 min. cure)
4. Attain a bond to metal			
after 30 sec.	5	99	98
after 5 min.	100	530	369
5. Total capsular adhesive stability -----			9 months
DMT/Polyester Capsules -----			22 months
BPO/Epoxy Capsules -----			9 months

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SECTION I

INTRODUCTION

This report describes the research conducted during a one year extension of the contract for the Development of Multipurpose Capsular Adhesive Systems, Picatinny Arsenal Contract DAAA 21-68-C-0581. The contract is under the joint sponsorship of both the U.S. Army Picatinny Arsenal and The U.S. Naval Ordnance Laboratory.

An unsaturated polyester-epoxy adhesive system was formulated during the first year of study.¹ This adhesive developed is a two component system which can be prepared as a dry total-capsular system by encapsulating both components, or as a "paste" system by encapsulating component A and blending the capsules of this ingredient into the resinous component B. Each component is made up of several ingredients. Component A is primarily an unsaturated polyester resin to which a free-radical accelerator and a filler are added. Component B is an epoxy resin which contains a generous amount of a peroxide curing agent. When the components are mixed the peroxide-polyester reaction takes place instantaneously.

The work carried out during the program extension was directed toward the characterization of the adhesive systems. The efforts were concentrated in four areas: (1) determination of long term adhesive stability relative to temperature and humidity storage limitations of the components; (2) addition of a thixotropic agent to the formulation; (3) development of a mechanical device for application of the adhesive to a substrate for bonding; and (4) conduct adhesive component encapsulation scale-up studies.

In addition to the studies listed above, bonding studies were conducted on barnacle fouled surfaces, on steel boiler plate and on other submerged substrates. In order to effect improvements in the strengths of the bond to certain specific substrates some reformulation and modification of the adhesive was also accomplished.

¹ "Development of Multipurpose Capsular Adhesive Systems - Interim Summary Report," Tech. Rpt. 3895, U.S. Army Picatinny Arsenal

SECTION II

TECHNICAL DISCUSSION

During the conduct of the initial phase of this program, that is, the development of a multipurpose capsular adhesive, a great number of things were learned and a functional adhesive was developed. In order that this adhesive might be optimized for specific end-use applications and also so that the adhesive might be characterized, NCR was requested to extend and expand the studies into four specific areas. These study areas are as follows:

- A. Adhesive Stability - The objective here was to conduct an extensive shelf-life stability program on the adhesive ingredients in order to determine their storage limits under various temperature and humidity conditions.
- B. Thixotropic Agents - The objective was to conduct research to determine if a thixotropic agent could impart better homogeneity to the paste adhesive.
- C. Mechanical Applicator - A natural follow-on to the development of an adhesive in capsular form is the development of a method of application. Since this adhesive is to be used in underwater environments and on many substrates a device for a device for rupturing the capsules, ejecting the adhesive and applying it to a substrate for bonding is desirable. The objectives were to provide a device consisting of a chamber into which the adhesive or a sealed cartridge containing the adhesive may be loaded; and a piston or other device to supply a force to rupture the capsules, mix the adhesive and expel it from the chamber and eject it onto the substrate. The device must be suitable for underwater use, and the packaging of the paste adhesive for use in the applicator must be accomplished with a disposable container.
- D. Scale-Up - The objective was to conduct batch-size scale-up to produce larger quantities of capsules for evaluation studies and to determine if large size capsules can be prepared in quantity.

The work conducted to achieve the objectives outlined above is presented in the following paragraphs. In addition to the studies outlined it became necessary during the conduct of the program to conduct bonding studies to various substrates and to reformulate and modify the adhesive to affect better bonds to certain of the substrates. These studies are also discussed in the following paragraphs.

A. Adhesive Stability

The adhesives developed during the first phase of the program was a two component, multi-ingredient system. The components consisted of the following constituents:

<u>Component A</u> <u>Polyester Portion</u>		<u>Component B</u> <u>Epoxy Portion</u>	
Resin	Aropol 7240 MC	Resin	ERL 4221
Accelerator	dimethyl paratoluidine	Initiator	Benzoyl peroxide
Filler	TiO ₂		

When mixed together in the proper ratios these ingredients provide a rapid curing polymeric compound with unique adhesive properties. In the adhesive systems developed these components are both encapsulated in the "capsular" adhesive and component B is encapsulated and the capsules suspended in Component A in the "paste" adhesive. The stability studies, therefore, consisted of an examination of each of the components separately and as a total adhesive.

In order to determine the shelf life of the adhesive and of each of its components samples of each batch formulated were placed in storage and examined periodically to determine their functionality and retention of original physical characteristics. In total, several hundred individual samples and many formulations have been evaluated. The general results of these evaluations are presented below.

Polyester Component	stable for 22 months
Epoxy Component	stable for 9 months
Total Capsular Adhesive	stable for 9 months
Capsular Paste Adhesive	stable for 9 months

In compiling the shelf-life stability of the various adhesive systems and formulations it was noted that a number of individual samples either changed in functionality or physical characteristics at what appeared to be random time intervals or with little or no predictability. Since certain samples maintained their original properties it became clear that certain factors were influencing the stability of specific samples. In ensuing studies the major factors affecting the stability of each component and of the formulated adhesive systems were identified and the necessary steps to provide maximum stability were taken.

In this section each component and the total adhesive are discussed separately. The major factors affecting the stability of each component are also identified and discussed.

1. Polyester Component

The polyester component has been proven to be the most stable component of the adhesive system. The primary problems associated with this component have been due to loss of the dissolved styrene in the resin and its sensitivity to ultraviolet light. Stability studies have been conducted on this component both in capsular form and in liquid form (for use as a paste adhesive). The results of these evaluations are presented in this section.

a. Capsule Stability

The polyester resin (Aropol 7240MC) and accelerator/polyester resin mixture (DMT/Aropol 7240MC) have been subjected to ambient aging tests for 22 months. The capsules were stored in glass vials and stored in an ambient environment where temperatures ranged from 60°F to 100°F and relative humidity varied from 50 to 90%. The individual vials were stored in dark cabinets and in direct sunlight. Capsules containing 1% to 10% dimethyl paratoluidine (DMT) in Aropol 7240MC did not deteriorate over the entire test period.

During the program reformulation was done to accommodate dispenser usage of the adhesives. A slower setting adhesive based on a slower initiator, diethyl aniline, (DEA) was developed and the accelerator/polyester resin (DEA/Aropol 7240MC) portion of the adhesive was evaluated re its stability. Initial studies indicated that the DEA/Aropol 7240MC mixture was susceptible to exposure to direct sunlight. Because of this a series of stability tests were initiated. The encapsulated formulation of 5% DMT/Aropol 7240 MC was used as a standard since several months of stability had already been achieved in laboratory environment.

The following samples were prepared for comparative evaluations:

Sample A - Encapsulated Polyester Resin Component

5% DMT
5% TiO₂
90% Aropol 7240MC

Sample B - Encapsulated Adhesive

Polyester Component	5% DMT	2 parts
	5% TiO ₂	by weight
	90% Aropol	
Epoxy Component	12% BPO	1 part
	88% ERL 4221	by weight

Sample C - Encapsulated Polyester Resin Component

0.1% DEA
5% TiO₂
94.9% Aropol 7240MC

Sample D - Encapsulated Adhesive

Polyester Component	0.1% DEA	2 parts by weight
	5% TiO ₂	
	94.9% Aropol	
	7240MC	
Epoxy Component	12% BPO	1 part by weight
	88% ERL 4221	

Each sample was divided into four aliquots and packaged as follows:

open pan
clear vial
amber vial
sealed can

Each aliquot was subdivided and sample were prepared for aging studies in three environments:

laboratory bench top
dark cabinet
fadometer

A fadometer is an apparatus which directs ultraviolet light, produced from a carbon arc, onto a target area in which the test samples are placed. During operation the sample chamber normally experiences a temperature of 40 to 50°C. Exposure to ultraviolet light in the fadometer for one hour is equivalent to exposure to direct sunlight for 5 days.

Fadometer test results are presented in Table I and the laboratory bench top environment test results are in Table II. Test results on samples stored in a dark cabinet show all samples to be stable for the duration of the test. Any thickening of the capsule internal phase or total cure was the criteria used to determine the effect of the test environment.

Results of the fadometer tests would indicate that the encapsulated DMT/polyester resin mixture is as unstable to light as the encapsulated DEA/polyester resin mixture. However, ambient tests show that only the DEA/polyester resin mixture is unstable. All DMT/polyester resin capsules were stable for the 8 week test period, with previous tests showing the DMT/polyester capsules to be stable for up to 22 months under normal laboratory conditions. There is apparently a threshold level of ultraviolet light-temperature combination which initiated the DMT/polyester mixture. This was evidently reached in the fadometer but is not experienced in ambient environments. The DEA polyester resin mixture is sensitive to ambient and accelerated light aging. Amber vials, which filter out the ultraviolet light can be used as a means to increase the shelf-life of the DEA/polyester capsules. There is a possibility that the yellow color imparted by the DMT in the DMT/Aropol 7240MC resin mixture (which is a more active accelerator) also filters out the ultraviolet light, thus stabilizing this adhesive component.

Table I - Fadometer Test on Capsular Adhesive Components

<u>Type Container</u>	<u>Time of Test (hrs)</u>	<u>Samples</u>			
		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
pan	1	Capsule IP Dry	Capsule IP Dry	Most Cured	Some Cured
	2	Cured	Cured	Cured	Cured
clear vial	1	Uncured	Uncured	Uncured	Uncured
	2	Uncured	Uncured	Uncured	Uncured
	3	Partial Cure	Partial Cure	Uncured	Uncured
	4	Partial Cure	Partial Cure	Uncured	Uncured
	5	Partial Cure	Partial Cure	Cured	Cured
	19	Cured	Cured	Cured	Cured
amber vial	1	Uncured	Uncured	Uncured	Uncured
	2	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Uncured	Uncured
	4	Uncured	Uncured	Uncured	Uncured
	5	Uncured	Uncured	Uncured	Uncured
	19	Uncured	Uncured	Uncured	Uncured
can	38	Uncured	Uncured	Uncured	Uncured
	1	Uncured	Uncured	Uncured	Uncured
	2	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Uncured	Uncured
	4	Uncured	Uncured	Uncured	Uncured
	5	Uncured	Uncured	Uncured	Uncured
	19	Uncured	Uncured	Uncured	Uncured
	38	Uncured	Uncured	Uncured	Uncured

Table II - Ambient Tests on Capsular Adhesive Components*

<u>Type Container</u>	<u>Time of Test (weeks)</u>	<u>Samples</u>			
		<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
pan	1	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Uncured	Uncured
	5	Uncured	Uncured	Partial Cure	Partial Cure
	6	Uncured	Uncured	Cured	Cured
clear vial (in window)**	1	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Partial Cure	Partial Cure
	5	Uncured	Uncured	Cured	Cured
clear vial	1	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Uncured	Uncured
	5	Uncured	Uncured	Partial Cure	Partial Cure
	6	Uncured	Uncured	Partial Cure	Partial Cure
	8	Uncured	Uncured	Cured	Cured
amber vial	1	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Uncured	Uncured
	5	Uncured	Uncured	Uncured	Uncured
	6	Uncured	Uncured	Uncured	Uncured
	8	Uncured	Uncured	Uncured	Uncured
can	1	Uncured	Uncured	Uncured	Uncured
	3	Uncured	Uncured	Uncured	Uncured
	5	Uncured	Uncured	Uncured	Uncured
	6	Uncured	Uncured	Uncured	Uncured
	8	Uncured	Uncured	Uncured	Uncured

*Tests conducted in the open laboratory environment away from windows

**Sample placed in window in direct sunlight

b. Unencapsulated Component Stability

In addition to the tests on encapsulated polyester resins, tests were also conducted on the unencapsulated polyester resin and accelerator/resin mixtures with the following samples prepared:

Sample 1	Aropol 7240 MC
Sample 2	5% DMT
	95% Aropol 7240 MC
Sample 3	5% DMT
	5% TiO ₂
	90% Aropol 7240 MC
Sample 4	0.1% DEA
	99.9% Aropol 7240 MC
Sample 5	0.1% DEA
	5% TiO ₂
	94.9% Aropol 7240 MC

Test results are presented in Table III. The results indicate that the accelerator/polyester resin mixture is more stable to light than the resin alone. Also, addition of TiO₂ (a filler in the adhesive system) further stabilized the resin mixture. However, when a large amount of TiO₂ was used (paste system), sufficient to mask the yellow color of the DMT, the resulting mixture was less stable in the presence of light.

Therefore, it is recommended that all capsular adhesive formulations, whether DMT, DEA or other accelerator be stored in amber containers to assure light stability.

2. Epoxy Component

In conducting the stability studies, erratic results were obtained on the Benzoyl peroxide (BPO) ERL 4221 capsule component. This component, which is encapsulated in all formulations, demonstrated a marked decrease in stability as the concentration of BPO was increased to the 20% level. The decrease in stability, first found in the paste systems, was traced to the rupture of a percentage of individual capsules due to the development of needle like BPO crystals within the capsules.

The capsule instability was eventually traced to several causes the most significant of which are: a) variations in the resin as received from the supplier; b) variations in the capsule drying procedure and; c) the concentrations of benzoyl peroxide present and the form of the recrystallized BPO.

Table III - Fadometer Tests on Unencapsulated Polyester Component

<u>Type Container</u>	<u>Time of Test (hrs)</u>	<u>Samples</u>				
		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
pan	0.25	Tacky	Tacky	Tacky	Tacky	Cured
	1	Cured	Cured	Cured	Cured	Cured
clear vial	1	Partial Cure	Uncured	Uncured	Uncured	Uncured
	2	Cured	Uncured	Uncured	Cured	Uncured
	18	Cured	Cured	Partial Cure	Cured	Cured
amber vial	1	Uncured	Uncured	Uncured	Uncured	Uncured
	2	Uncured	Uncured	Uncured	Uncured	Uncured
	18	Uncured	Uncured	Uncured	Uncured	Uncured
can	1	Uncured	Uncured	Uncured	Uncured	Uncured
	2	Uncured	Uncured	Uncured	Uncured	Uncured
	18	Uncured	Uncured	Uncured	Uncured	Uncured

a. Capsule Deformation (A statement of the problem)

In the development of the capsular adhesive, formulations utilizing concentrations of 10% to 20% benzoyl peroxide in ERL 4221 epoxy resin were evaluated both for reactivity and stability. In the course of these studies samples of all concentrations within this range were tested and found to be stable for periods up to nine months. After nine months, regardless of the concentration of BPO present above 10% the capsules begin to exhibit a viscosity increase. Once this occurs the capsules become completely hardened within two or three weeks.

A nine month shelf-life had been established rather early in the program extension when capsules containing 20% benzoyl peroxide began to exhibit drastically reduced stability. A microscopic examination of the capsules revealed that the benzoyl peroxide had formed long, needle-like crystals within the capsule walls. These crystals caused the capsules to deform and in some cases actually pierced the wall causing premature mixing and curing of capsular paste adhesives.

Figure 1 illustrates the problem. In Plate 1 a large crystal of BPO has deformed a capsule while Plate 2 shows an undeformed capsule. In Plates 3 and 4 the BPO crystals have clearly penetrated the capsule walls. There is a clear undeformed capsule on the left in Plate 3 showing that the phenomenon is not present in all capsules. In fact the deformation is only present in about 25% of the capsules in any batch and has only appeared in 20% BPO formulations.

b. Concentration Adjustments and Encapsulation Studies

At ambient temperatures approximately 10 percent of benzoyl peroxide can be solubilized in ERL 4221 epoxy resin. The 12, 14, 16 and 20% BPO/ERL 4221 epoxy resin components have all been saturated solutions when encapsulated. When preparing a batch of epoxy resin component for encapsulation it has been customary to first completely dissolve the BPO in the epoxy resin by heating to a temperature approaching 55°C for the maximum concentrations. (20% BPO in epoxy resin) The encapsulation temperature is approximately 55°C initially and the encapsulation is simplified using solutions rather than dispersions.

In all encapsulations using concentrations of 16% or less BPO in Epoxy, crystal growth has not been a problem. In encapsulating 20% BPO solutions the capsule deformation problem appears in certain batches. When the capsule deformation does not occur nine month stability and optimum adhesive properties are achieved.

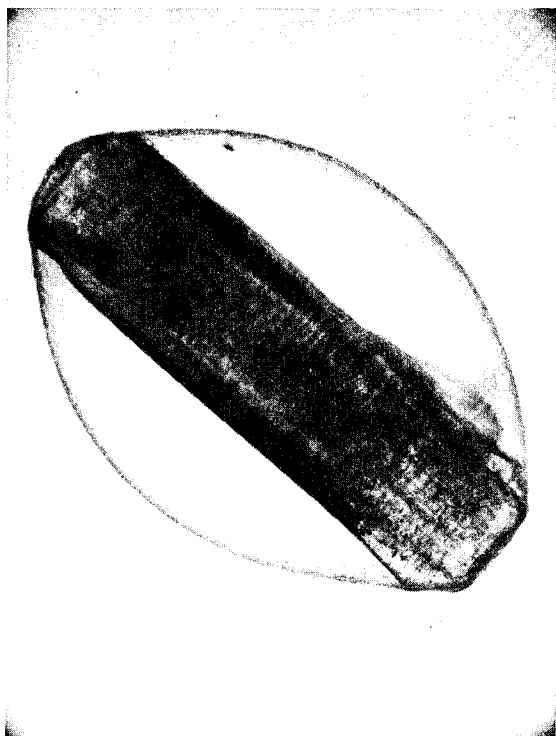


Plate 1



Plate 2

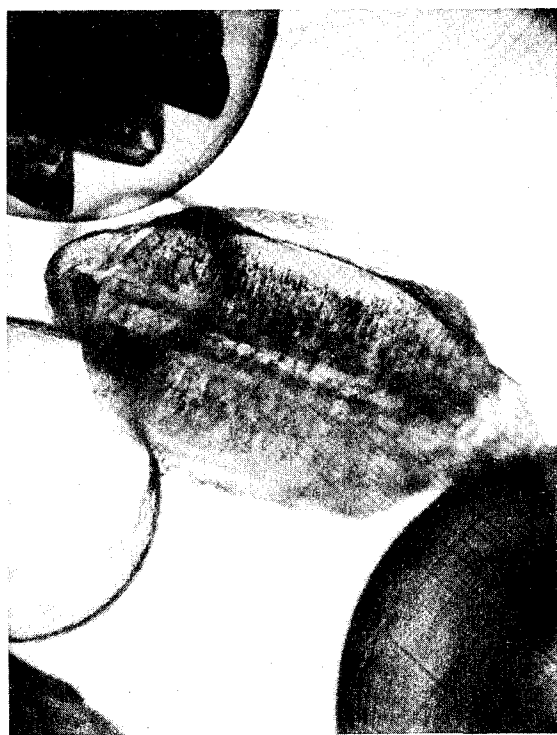


Plate 3



Plate 4

Figure 1. Micrographs of BPO/ERL 4221 Capsules

In an effort to determine the cause of the needle-like crystals in certain batches of ERL/BPO (20%), the following parameters were monitored:

- . maximum temperature of BPO/ERL
- . rate of dissolution of BPO in ERL
- . origin and form of BPO (powder-crystal)
- . encapsulation technique
- . encapsulation parameters
- . lot and batch of ERL

Each of these parameters proved to have no effect upon the growth of BPO capsules with the exception of the lot and batch of ERL. Since early attempts to determine the batch to batch differences in the ERL were fruitless the maximum concentration of BPO that could be tolerated without capsule deformation problems was established at 16%. This allows the highest possible BPO concentration and empirically solves the capsule deformation problem.

c. Epoxy Resin Variations

ERL 4221 is a peracetic acid type epoxy resin. In the synthesis of the monomer a certain amount of the acetic acid is not completely removed. The amount of acid is small and for all practical purposes does not pose a significant problem. However, if the monomer is allowed to age for long periods of time the available carboxylic acid will react with the oxirane ring causing a change in functionality.

During the first year of this program there was an interruption in the supply of ERL 4221 resin due to an explosion of the reactor used to prepare the monomer. In order to supply customers Union Carbide depleted its inventory. The plant has only recently gone back on stream, producing fresh monomer.

Since the plant is back on stream, a batch of this monomer was received and it was compared to several of the previous batches, both as an encapsulant containing 20% BPO and for its chemical and physical properties. A comparison of significant properties is presented in Table IV.

Based on this information it becomes readily apparent that the acetic acid is being depleted in the samples. The manufacturer has indicated that the resin will color as the acetic acid reacts but that this is not a problem with fresh material. In any case it is now possible to write a specification to assure uniformity of raw material which will provide stable capsules.

Table IV - Properties of Batches of ERL 4221

<u>Batch No.</u> <u>Specification</u>	<u>Date</u> <u>Received</u>	<u>Acid</u> <u>Number</u>	<u>Co-Pt</u> <u>Color</u>	<u>Visual</u> <u>Color</u>	<u>Epoxide</u> <u>Number</u>	<u>20% BPO</u> <u>Capsule Stability</u>
Specification	- -	0.10	100 (max.)	clear	11.9	- -
0114-RT	July, 1970	0.07	25	clear	11.65	excellent
9089-DM	April, 1968	0.05	20	clear	11.63	excellent
0092-DK	Jan., 1970	0.05	70	yellow	11.59	fair
9177-RT	April, 1969	0.03	80	amber	11.44	poor

d. Drying Procedure Variation

After encapsulation of the BPO/epoxy resin mixture, the capsules are separated from the encapsulation media by filtration. The wet capsules are then placed in a fluidized bed dryer. Generally heat is applied to facilitate drying. The inlet air temperature of the drying apparatus is maintained at about five degrees centigrade above room temperature. The outlet air temperature is about 10°C lower than the inlet air temperature due to the evaporation of moisture from the surface and wall structure of the capsules. As the capsules dry the outlet temperature increases as the evaporation rate decreases, and when the outlet and inlet temperatures equilibrate the capsules are presumed to be devoid of removable moisture.

Both laboratory and pilot plant batches of BPO/Epoxy capsules are normally dried on fluid bed driers. On several occasions it has been necessary to provide inlet air at temperatures well in excess of 30°C in order to facilitate the drying of the capsules. This was due to laboratory and pilot plant conditions in which ambient temperatures were 30°C or higher.

The capsules which resulted from these elevated inlet temperature drying cycles exhibited excessive permeability and have a characteristic yellow-tan color.

Adhesion tests carried out using batches dried at elevated temperatures indicate that the reactivity of adhesives formulated with these capsules is deficient. Ambient temperature, therefore, will no longer be used as a criteria for inlet and outlet drier air temperatures. A maximum inlet and outlet temperature of 25°C will be established for all future fluid bed drier runs.

3. Total Capsular Adhesive Stability

The total capsular adhesive system can only be as stable as its least stable component. Studies on the individual components indicate that the polyester component is stable for at least, if not more than, 22 months, while the epoxy component is only stable up to nine months. Therefore, the total adhesive stability is limited to nine months.

Dry state permeability tests (DSP) were conducted on three total capsule adhesive samples in order to determine the stability of the mixed capsular adhesive in ambient environments. Results of these tests are presented in Figure 2.

Sample one is formulation CA-13K (5-20); sample two is formulation CA-13K (5-20) made up of polyester capsules known to be of poorer quality than standard polyester batches; and sample three is CA-13L (01-12) which is the slower reacting adhesive system using DEA as an accelerator.

The initial weight loss of samples 1 and 3 in the first four days is due to loss of residual water in the capsule wall. There is little or no loss of weight over the remaining test periods for these two samples indicate that these formulations are quite stable. However, sample 2, known to be poor, continued to lose weight, due to the loss of styrene from the polyester, and illustrates that poor capsules will exhibit permeability. Even though sample two is of poor quality, it still only loses a little over 1% of its weight in 25 days.

The effect of humidity on the capsular adhesive was evaluated by placing samples in a desiccator maintained at 75% relative humidity and weighing the samples periodically. Any gain or loss of weight was recorded. The results of these evaluations are presented in Figure 3. The weight gain by the total capsular system is substantial. In the high humidity environment, the capsule wall absorbs moisture and swells, thereby increasing the weight of the sample. However, because of the two capsule system, there is more involved than just water absorption. During the test period, the peroxide/epoxy capsules changed color from white to a yellow brown while the polyester capsules became lighter in color, from yellow-brown to pale yellow. The resulting aged adhesive capsule sample was completely unreactive when tested for cure rate and bond strength.

Adhesive deactivation can be caused by deactivation of the BPO in the epoxy resin. It is postulated that a portion of the DMT carried by the volatile styrene monomer from the polyester resin permeated the swollen wall of the polyester capsules, and reperfused the swollen wall of the epoxy capsule, subsequently reacting with the BPO and thus deactivating the adhesive reaction initiator.

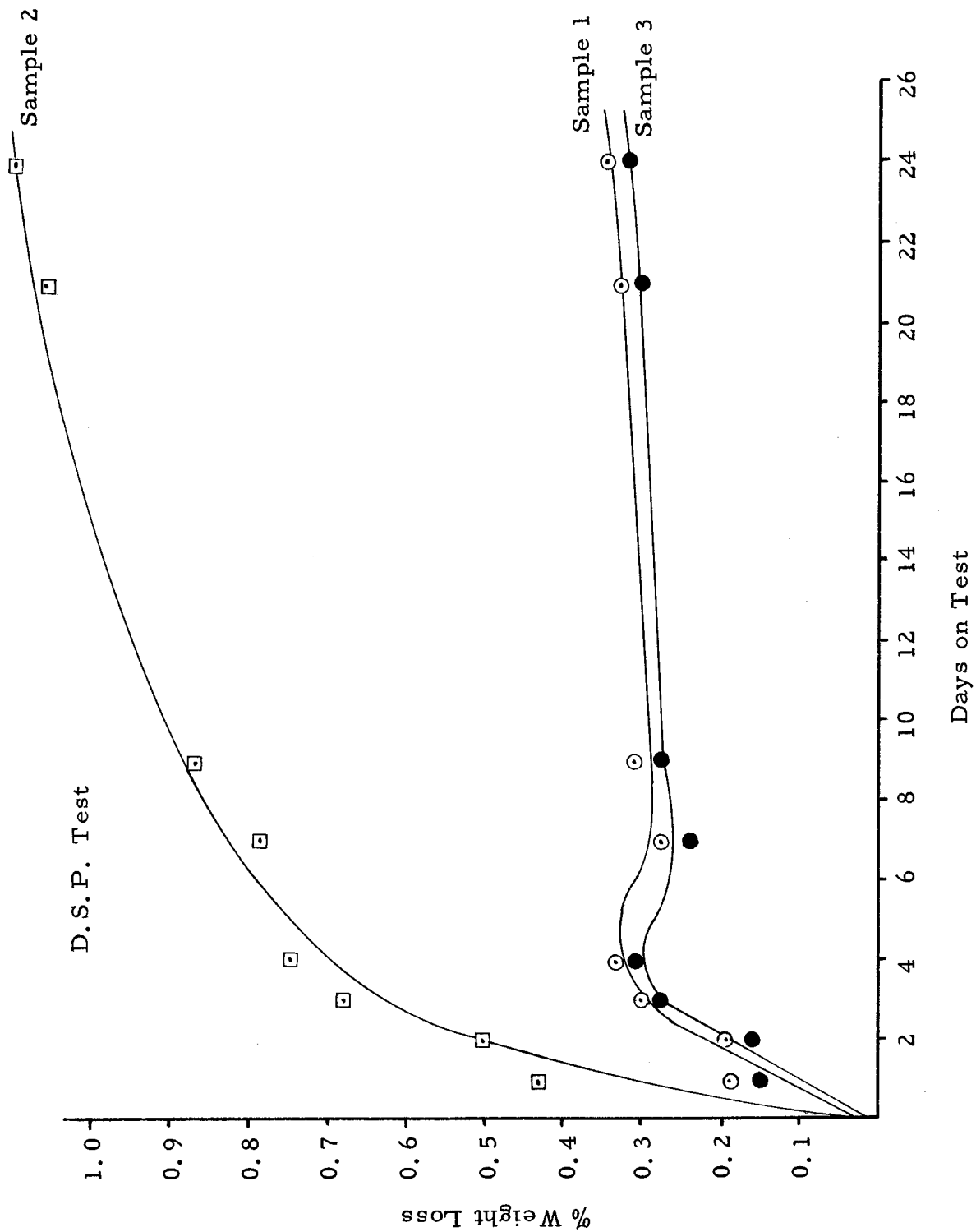


Figure 2

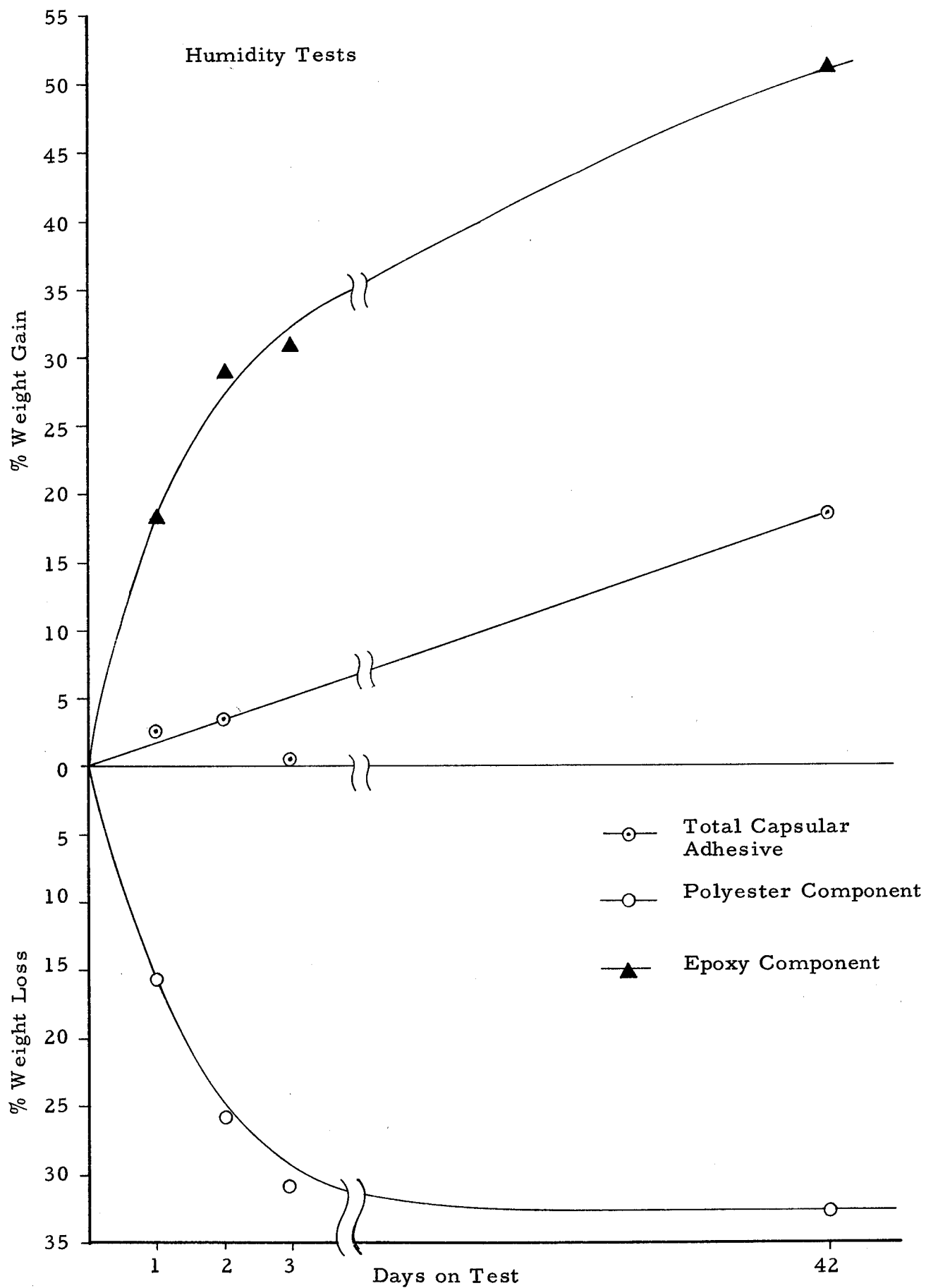


Figure 3

Additional tests were initiated to substantiate this phenomena. Capsules of each component (DMT/polyester and BPO/epoxy) were weighed separately and placed at opposite ends of the same high humidity chamber. The samples were reweighed periodically. Results of these tests are presented in Figure 3.

The DMT/polyester sample exhibited a large weight loss, while the BPO/epoxy showed a significant weight gain. This indicated a transfer of some of the component from the polyester capsules to the BPO/epoxy capsules which resulted in eventual deactivation of the BPO.

These tests were conducted in a rather small, closed system (desiccator). The DMT/styrene, permeating from the swollen polyester capsule wall, produces a vapor pressure in the container which then accelerates the re-permeation of the DMT/styrene through the swollen wall of the BPO/epoxy capsules.

Adhesive samples placed in an open system under high humidity conditions, are deactivated only when the two capsules are in physical contact; and then, the rate of deactivation is not as great as those tested in the desiccator because the DMT/styrene permeation driving force is reduced.

B. Adhesive Formulation Refinements

The adhesive formulation developed during the first year of the contract possessed the desired characteristics of reactivity, bond strength and stability. However, the paste system exhibited a tendency to separate. Studies were initiated to find a thixotropic agent that could be added to the "paste" adhesive to better improve the suspension qualities of the BPO/epoxy capsules in the polyester resin. Also, it became necessary during the course of adhesive stability studies to consider slower reacting adhesive formulations to insure stability of the capsular adhesive.

1. Addition of Thixotropic Agents

Aropol 7240MC with 5% DMT dissolved in it is not a very viscous liquid. Even with the addition of titanium dioxide as a filler, the viscosity of the mixture is not increased enough to hold the BPO/ERL 4221 capsules in suspension. In these systems the epoxy capsules tend to settle to the bottom of the container upon standing.

Various thickeners were investigated to improve the suspension characteristics of the adhesive system. Many thickeners recommended for use with Polyester resins were tried and gave thick suspensions. However, all either gelled or cured the DMT/Aropol 7240 mixture.

Resins, not specifically recommended for polyester resins were also tried, but results were poor. In most cases, a great quantity of the resin was required to increase the viscosity of the DMT/Polyester mixture.

Table V - Effect of Thickeners on Paste Adhesive Stability

<u>Polyester Thickness</u>	<u>Resin Stability - Cured Properties</u>
Parlen P-20	- cured resin
Parlen S	- cured resin
Carbol	- gelled - poor strength
Epolene	- gelled - poor strength
Elvax	- gelled - poor strength
Asbestos	- good suspension poor strength
Vinyl copolymers	- good suspension good initial strength lowered ultimate strength

Even then, the suspension characteristics of the thickened polyester mixture were very poor. Those resins which gave very desirable suspension, also cured the DMT/Polyester mixture upon standing several days.

Of all materials tested, asbestos and various vinyl coating powders showed the most promise as thickening agents while maintaining a stable mixture.

a. Asbestos

Two types of asbestos were obtained from Union Carbide for evaluation as thickening agents for the adhesive "paste". The grade which exhibited greatest promise is a pure resin asbestos (Calidrin RG-244). When the powdered asbestos is added at 2 percent by weight to the polyester resin, it effectively thickens the polyester resin. When the BPO/ERL capsules are added to the thickened resin, the capsules are maintained uniformly in suspension.

The asbestos has been tested in polyester resin containing 5 percent DMT for over six months with no indication of polymerization in the resin. Other grades of asbestos powders have been tested in the polyester/DMT mixture, but they usually induced polymerization of the resin. A number of asbestos samples were found to be stable in the polyester resin as long as the DMT was not present. In the initial tests with RG-244 asbestos, some polymerization of the polyester resin/DMT was observed, but this was probably due to the fact that the samples were stored near the laboratory windows in clear glass containers and the polymerization was initiated by the light.

b. Vinyl Coating Powders

A reference was found in Chemical Abstracts¹, which suggested the use of vinyl polymers as thickening agents for polyester resins. A series of vinyl coating powders was available from Union Carbide Corp. for evaluation. The powders consisted of polymers and copolymers of vinyl chlorides and vinyl acetates. After evaluating several of the powders, one was selected that is a copolymer of vinyl acetate and vinyl chloride, known as VYLF. When 20 percent of VYLF by weight was added to a 5 percent solution of DMT in Aropol 7240CM a very viscous solution was formed. When capsules of BPO/ERL were added to the solution they were maintained in suspension.

¹ Chemical Abstracts, Vol. 67 (1967) No. 18, page 7821, 82775b.

A paste adhesive system was prepared with the vinyl powder to obtain bond strength data. The formulation was coded CA-15V (5-20) and had the following composition:

<u>CA-15V (5-20)</u>	<u>Percentage</u>
Aropol 7240MC	46.4
DMT	2.4
VYLF vinyl powder	12.2
TiO ₂	14.6
20% BPO/ERL capsules	<u>24.4</u>
	100.0%

The tensile values for this formulation on dry steel were:

150 psi at 1 minute
350 psi at 5 minutes
350 psi at 10 minutes

It was determined that the adhesive had a maximum bond strength of 350 psi regardless of cure time.

The vinyl copolymer gave some flexibility to the cured adhesive system, which is a most desirable property.

2. Reformulation Studies of Capsular Adhesives

Formulation CA-13K (5-20) has been thoroughly tested with respect to cure time, bond strength, stability, and ease of production. Test data show that this adhesive system produces fast cure times and excellent bond strengths. However, studies conducted during the program indicated problems in stability and reproducibility of the 20% BPO/epoxy component as to its reactivity in the total adhesive system, and as an adhesive which can be extruded from an appropriate dispenser. Therefore, adhesive systems with reduced cure rates were studied because they offered greater stability with more reproducible capsule preparation and somewhat greater ease of mixing, application and working time.

A list of adhesive systems and their cure times and bond strengths is presented in Table VI. The slower reacting systems yield lower bond strengths initially but ultimate bond strengths are generally greater than ultimate bond strengths obtained on the faster system CA-13K (5-20).

To enhance initial tack of the adhesive, a vinyl chloride-vinyl acetate copolymer can be added. The addition of the copolymer increases the viscosity of the polyester component of the adhesive and improves the suspension of the titanium dioxide filler in the polyester resin. With an increase in tack, the bond strengths during initial cure are greater. This is evidenced when comparing formulations CA-13K (5-20) V and CA-13K (5-20). However, ultimate bond strengths of formulations containing the vinyl copolymer are not as high as those formulations without the copolymer.

Table VI - Various Adhesive Formulations and Their Bond Strengths

Cure time (min)	Tensile Strength on Steel to Steel (PSI)										Shear Strength on Al to Al (PSI)				
	Underwater					Dry					Dry				
	1/2	1	5	1/2	1	5	15	30	60	16 hr	1	5	60	5 days	
Formulation															
CA-13K (5-20)	98	197	369	80	198	562	-	-	-	-	74	167	-	568	
CA-13K (5-20)V	-	-	-	-	-	-	-	-	-	-	119	344	400	480	
CA-13K (5-12)	32	83	300	40	105	500	-	-	-	-	96*	410*	475*	590	
CA-13K (2-20)	34	116	436	42	114	554	-	-	-	-	40	260	-	557	
CA-13K (2-12)	13	40	330	30	69	470	-	-	-	-	-	-	-	562	
CA-13K (1-12)	-	-	-	-	-	-	-	-	-	-	-	-	-	563	
CA-13L (01-12)	-	-	-	-	-	-	50	124	171	525	-	-	-	-	

*Al substrates were further prepared by cleaning with steel wool.
All other substrates tested were merely solvent washed.

The adhesive system CA-13K (5-12) appears to be close to an optimum system for most applications on this program. In addition the 12% BPO/epoxy capsules are more reproducible than the 20% BPO/epoxy capsules. Also, the system gave 5 to 15 seconds more working time after initiation before the adhesive sets. If higher initial bond strengths are desired (with a slight loss of ultimate strength) the vinyl copolymer can be added to the system.

3. Addition of Aliphatic Azo-Nitriles

When the reduction in the peroxide concentration created a cure rate problem, it was decided to consider another approach. Since the peroxide could not effectively be reduced without loss of cure rate, it seemed logical to substitute another free-radical initiator for a part of the benzoyl peroxide. The azo-nitrile initiators were investigated to determine if this approach would produce the desired results. It is also desirable to have a secondary initiator in the formulation to improve the polymerization propagation. In the rapid curing adhesive system there is evidence that the free-radical propagation is limited to the immediate area surrounding the benzoyl peroxide. It is theorized that the heavy excess of peroxide required for the fast cure is resulting in premature polymer termination.

Since the azo-nitrile compounds are dependent on external heat for their initiation of free-radical polymerization, only a part of the benzoyl peroxide can be replaced by the 2, 2' azobis (2-methyl propionitrile). In the adhesive system the azo-nitrile polymerization will be initiated by the exotherm from the redox reaction between the benzoyl peroxide and the dimethyl p-toluidine.

A batch of benzoyl peroxide/epoxy resin capsules was prepared in which 5 percent of the peroxide was replaced with 2, 2' azobis (2-methyl propionitrile) as a secondary initiator and also to reduce the peroxide percentage. The lower peroxide level eliminated any crystal growth in this batch.

The encapsulated 15% BPO/5% 2, 2' azobis (2-methyl propionitrile)/ERL 4221 was formulated into a test paste, CA-18A. When the adhesive was evaluated on a dead weight tester, 20 seconds were required to support a five pound weight 100% of the time. A normal formulation of CA-18A prepared from 20% BPO/ERL capsules will support a 5 pound weight 100% of the time in 15 seconds. Based on these tests, the 2, 2' azobis (2-methyl propionitrile) is not contributing to the reactivity of the adhesive. It is assumed that the azo nitrile is not being initiated by the exotherm from the peroxide decomposition reaction.

When the 2, 2' azobis (2-methyl propionitrile) was substituted for 3% of the benzoyl peroxide/ERL 4221 solution and evaluated in larger mass in a mechanical applicator, it contributed to the reaction. The total mass of adhesive that is contained, mixed and expelled from the mechanical applicator is about 75 milliliters. The total mass gets quite warm and there is sufficient heat generated by the exotherm from the peroxide to initiate the azo nitrile reaction. The azo nitrile contributed to the free-radical propagation.

The 2, 2' azobis (2-methyl propionitrile) will function as a free-radical initiator if the total mass of adhesive is sufficiently large. The thin layers of adhesive do not generate a great deal of total heat energy and the azo nitrile does not function. Since the crystal growth problem can be solved by other means it is not worth the inclusion of the azo nitrile in the encapsulated adhesive system since it is not likely that the paste adhesive will be used in sufficient mass to obtain initiation of the azo nitrile.

4. Other Epoxy Resins

A number of alternate epoxy resins have been tested as possible replacements for ERL 4221 as a solvent-carrier for the benzoyl peroxide. However, none of the epoxy resins evaluated were better solvents for the peroxide than ERL 4221. One epoxy resin that was comparable to ERL 4221 was 1, 3-bis (3-glycidoxypropyl) tetramethyldisiloxane, supplied by Dow Corning Corporation as XZ-5024. The resin was of particular interest because of the presence of the siloxane groups, which may improve the bond strength. Dow Corning XZ-5024 epoxy is amenable to encapsulation since it is insoluble in water. However, the bond strength is greatly reduced with the inclusion of this epoxy into the polyester adhesive system.

C. Adhesion Studies

Adhesion studies were conducted on various underwater substrates, including substrates covered with antifouling paint and barnacles. Long term aging studies were completed on bonded specimens to determine adhesion stability. Some difficulty was encountered when bonding to steel boiler plate in underwater environments, and a study program was established to effectively improve the bond strength to this substrate.

1. Underwater Aging of Bonded Specimens

Samples of the total-capsule and the "paste" adhesive systems were applied to various submerged substrates and allowed to age for 100 days. The following tensile strengths were obtained.

- (1) The total capsule system CA-13K (5-20) was applied to steel pads and bonded to submerged steel substrates. Of four samples, 2 samples showed adhesive failure on the pad and yielded results of 50 and 20 psi. The remaining 2 samples showed cohesive failure and gave values of 123 and 255 psi.
- (2) CA-13K (5-20) applied to steel pads and bonded to submerged concrete bricks showed adhesive failure on the brick. Three sample results were 0, 23 and 40 psi.
- (3) CA-13K (5-20) applied to steel pads and bonded to submerged creosoted wood gave very poor results. All three samples were easily dislodged with light pressure, showing adhesive failure on the pad.
- (4) The "paste" system CA-15A was applied to steel pads and bonded to underwater steel substrates. Of four samples tests, one showed adhesive failure on the pad. The three remaining samples were tested to 450 psi and held there for 5 minutes with no bond failure. The 450 psi is the limit of the tensile equipment.
- (5) CA-15A applied to steel pads and bonded to submerged concrete bricks. Two samples showed adhesive failure on the brick with results of 5 and 13 psi. The third sample showed cohesive failure with a tensile value of 53 psi.
- (6) CA-15A applied to steel pads and bonded to submerged creosoted wood gave poor values. Adhesive failure occurred on the creosoted wood with tensile values of 34, 36, 54 and 40 psi.

The best tensile values were obtained using CA-15A on the submerged steel substrates. All the other tests gave much lower tensile values. However, many of the lower values were due to grease or oil on the substrate prior to application of the adhesive pad. Cohesive bond failure, and adhesive bond failure on the substrate give true values as to the bonding and underwater aging of the adhesive system relative to the particular substrate. The underwater aging data is contained in Table VII for easy reference.

Table VII - Underwater Aging Studies*

<u>Formulation</u>	<u>Substrate</u>	<u>Tensile Values in psi</u>
CA-15A	Steel	45
		>450
		>450
		>450
	Concrete	5
		13
		53
	Creosoted wood	34
		36
		54
		40
CA-13K (5-20)	Steel	50
		20
		123
		255
	Concrete	0
		23
		40
	Creosoted wood	0
		0
		0
		0

*Duration of test - 100 days

2. Barnacle Bonding Test

A number of metal plates were shipped to NCR from the Naval Ordnance Laboratory Test Facility at Fort Lauderdale, Florida. The plates were coated with various types of paint and aged in the ocean so that various marine growth formed on the paints; the marine growth being principally barnacles. The metal plates were coated with three different types of paints, green Epoxy, red Vinyl Anti-Foul, and black Vinyl. Some of the plates were uncoated.

Adhesive formulation CA-18A was used to test the adhesion to the fouled paint samples. The adhesive was tested on steel to steel bonding at three minutes with bond strength values of 110 psi, 210 psi and 220 psi.

Table VIII - Adhesion to Barnacle Boiler Plate

<u>Red Vinyl Anti-Fouling Paint Test</u> ¹			
Sample	#1	33 psi	Cohesive and adhesive failure of paint.
	#2	61 psi	Heavy adhesive failure of paint from metal.
	#3	23 psi	Some adhesive failure of paint. A large section of barnacle shell remained on paint. There was no bonding of adhesive to the barnacle.
	#4	80 psi	Heavy adhesive failure of paint from metal.
<u>Black Vinyl</u> ¹			
Sample	#1	60 psi	About 50% adhesive failure of paint.
	#2	52 psi	Cohesive failure of paint.
	#3	38 psi	Heavy adhesive failure of paint from metal.
	#4	87 psi	Cohesive failure of paint, with some adhesive failure of paint to metal.
<u>Green Epoxy Coating</u> ²			
Sample	#1	80 psi	Adhesive failure from the epoxy coating.
	#2	12 psi	The substrate was covered with barnacle shell. There was very little bonding to the shell.
	#3	60 psi	Adhesive failure from epoxy paint. Some shell in glue line.
	#4	63 psi	Adhesive failure from epoxy paint. Some shell in glue line.

1 Boiler Plate Specifications - MIL P-15328 Pretreated - primer vinyl zinc chromate

2 Boiler Plate Specifications - MIL S-16113 Steelplate, high tensile - Hull and structural Class P-painted, descaled - abrasive or etched

Uncoated Metals ¹

Sample # 1	7 psi	Adhesive failure. Heavy shell coating.
	40 psi	Adhesive failure. Some shell.
	15 psi	Adhesive failure. Heavy shell.

In all cases where there was heavy barnacle coverage, the top of the shell was removed and the remains were filed down to a smooth layer in order to study the bonding to the shell. Very little bond was obtained to this shell, regardless of smoothness.

3. Steel Boiler Plate Adhesion

During the course of the program, problems developed when attempts were made to bond to steel boiler plates underwater. Various adhesive formulation revisions were made and special substrate treatments were carried out in an effort to improve the bond strength to the steel boiler plate. The following results were obtained:

Table IX - Adhesion to Steel Plate

<u>Treatment</u>	<u>Tensile Values (psi)</u>		
	<u>5 min</u>	<u>15 min</u>	<u>60 min</u>
Present adhesive system CA-13K (5-12)	60	80	-
Using a slower reacting adhesive gives slight improvement in bond strength			
CA-13K (1-12)	110	120	-
CA-13M (01-12)	-	-	250
Bond is improved by prewetting substrate with paste material (.4% DMT, 39.6% Aropol, 40% TiO ₂ and 20% ERL 4221)	125	235	-
Removal of oxide crust by sanding yields very little improvement	-	250	-
Acid etching of the steel substrate shows no improvement	-	205	-
Replacing TiO ₂ with various fillers (Al, Fe, FeO, ZnO, Zn) shows no improvement in bond strength	-	200	-
Additions of adhesion promoters, such as vinyl copolymer is unsatisfactory	-	150	-

In order to obtain optimum bond strength on any substrate, that substrate must be clean and free from foreign or loose particles. However, two major problems arose during the foregoing tests:

a) Boiler plate has a crust of iron oxide. For an adhesive to effectively bond to this substrate, it must completely wet the oxide crust and also penetrate that crust to the base metal. By using a slower reacting adhesive or by prewetting the substrate with a paste material prior to adhesive activation, bond strength is substantially increased.

¹ Boiler Plate Specifications - MIL P-15930 Class U unfinished - mill finish

b) Formation of the oxide crust is caused by oxidation of the plate in water, or an acidic environment. This problem cannot be overcome with the present adhesive systems. These adhesive systems, being acidic in nature and containing an oxidizer, possess all the ingredients for formation of the oxide crust. Even when adhering to base metal an oxide crust is formed by the reaction of the adhesive with the metal substrate in the underwater environment, and therefore the adhesive is only adhered to the oxide crust. The limit of bond strength of the adhesive is then the limit of bond strength between the oxide crust and the metal.

The best adhesion to the steel boiler plate is obtained by using formulation CA-13K (1-12) and prewetting the substrate with a paste. The following results were obtained on the steel boiler plate in underwater tests:

1 minute cure - 36 psi
5 minute cure - 125 psi
15 minute cure - 235 psi

These results are much lower than bond strength obtained on cold rolled steel in underwater tests, but tensile values are still greater than contract requirements.

D. Mechanical Applicator

Various mechanical application design ideas were evaluated for adhesive dispensage.

One design (Figure 4) consists of a cylindrical container that is fitted with a piston to force the capsule containing adhesive paste through a screen at one end of the container. There is also a wiper blade at the screen to assist in rupturing the activator capsules as the paste is forced through the screen. The design concept is very similar to a meat grinder.

The container is a one use item and contains an abundance of adhesive for each application. The containers are attached to a reusable motor to drive the shaft that operates the piston and wiper blade.

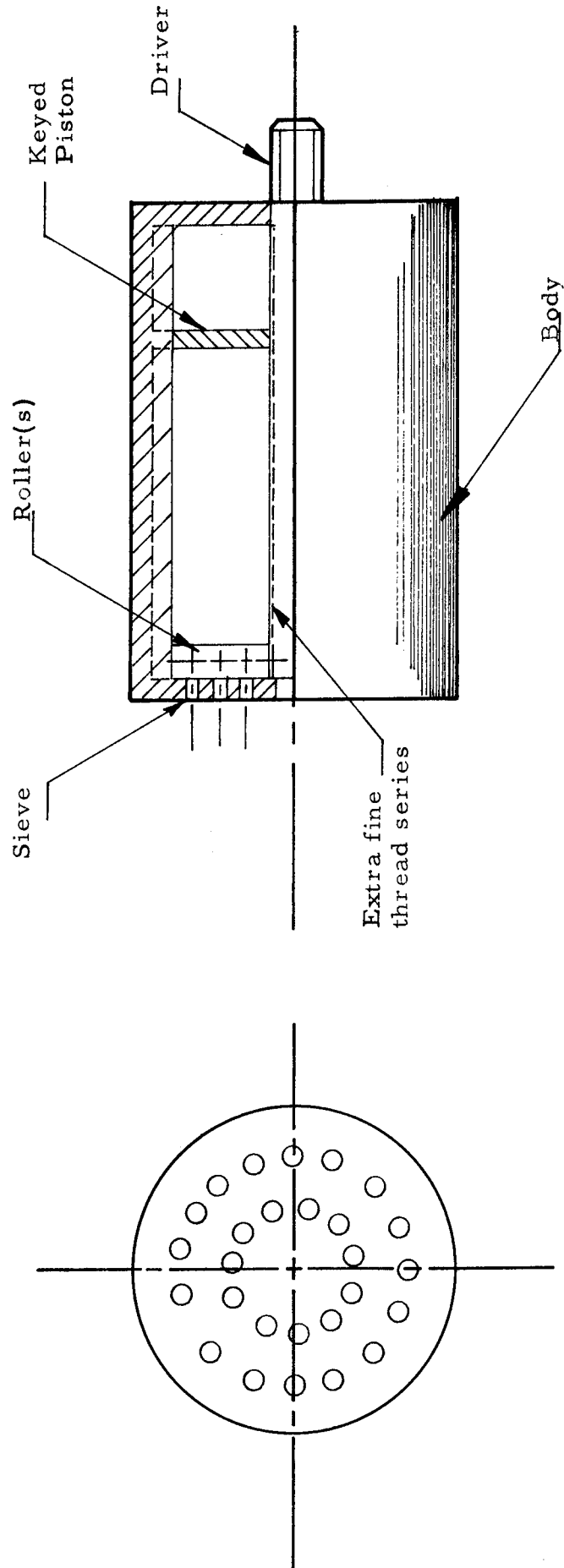


Figure 4. Conceptual Design of Adhesive Applicator

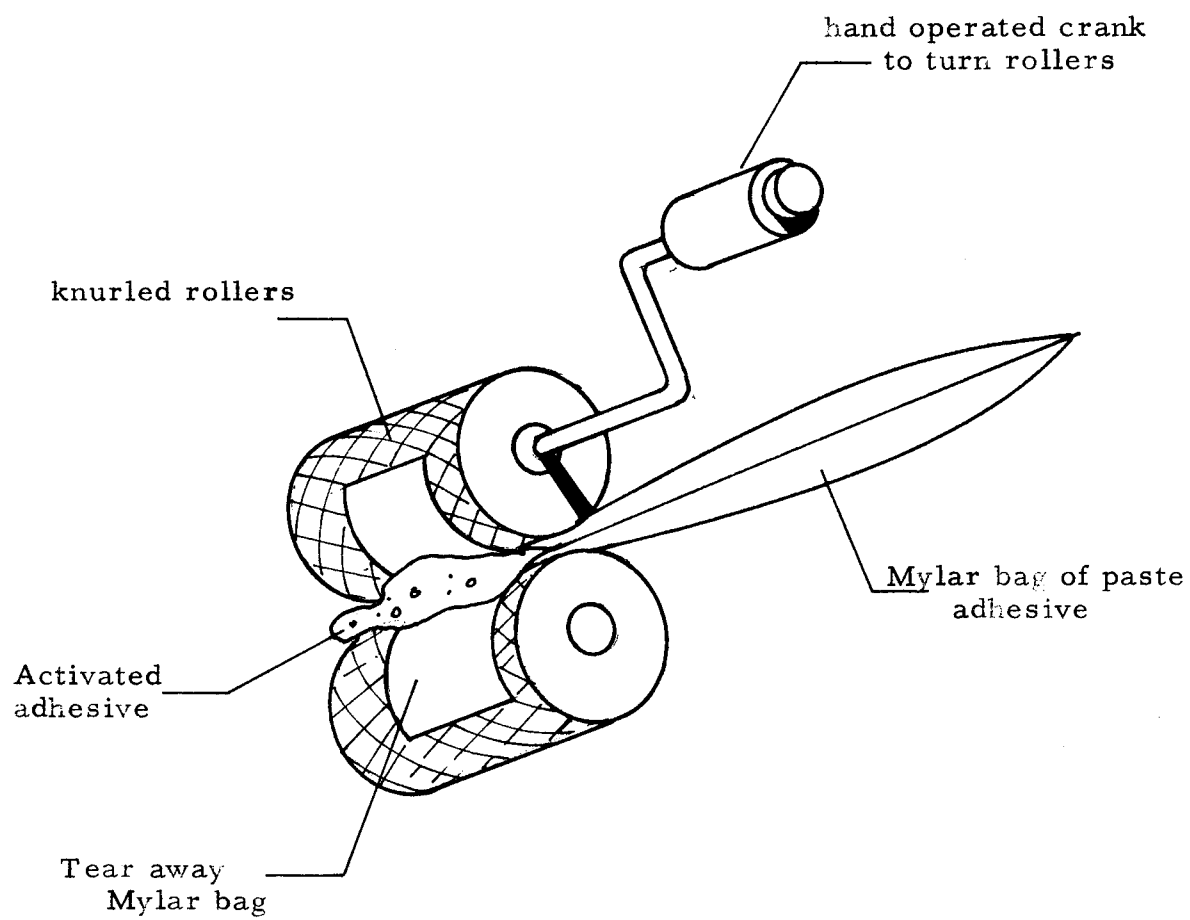
In the second concept (Figure 5) the capsule-paste would be packaged in a flexible bag. The activation mechanism would consist of two knurled rollers that the bag would be run through to rupture the capsules and activate the adhesive. When the bag emerges from the rollers the bag will be pulled away and the activated adhesive will pass through a tube and onto the application surface.

A number of Mylar bags of the adhesive paste were prepared and tested. The knurled rollers do an efficient job of rupturing the capsules and activating the resin when the viscosity of the paste and the spacing between the rollers is in the proper relation to each other. When the rollers are too close for a high viscosity paste, there is a tendency to force the paste toward the opposite end of the bag, away from the rollers.

To overcome the shortcomings of the previous designs, work was initiated on the development of a system to mix the adhesive components in their liquid states. Five milliliter disposable polypropylene hypodermic syringes were used as storage containers for the adhesive components. In order to have the 2:1 component ratio, the polyester resin component was dispensed from two five milliliter syringes and the BPO/ERL was dispensed from a single syringe. The hypodermic syringes were connected to a mixing chamber by a short section of 1/8" ID vinyl tubing. The mixing chamber consists of a length of 1/2" or 3/4" ID vinyl tubing. The concept is illustrated in Figure 6.

The adhesive flow within the mixing tube was restricted by several baffles within the tube, (pieces of bent wire and plastic plates were used). The baffles were positioned by securing the plates and wires to the chamber through small openings in the chamber wall. Each of the three streams of adhesive material had a surprising amount of cohesion, regardless of the amount of obstructions that were placed in the mixing chamber. Because of this cohesion a high percentage of the material would exit from the mixing chamber unmixed. When the obstructions in the mixing chamber were increased to the point that good mixing was obtained, a strong back pressure was observed.

Another mechanical application was fabricated that utilizes the adhesive components in their liquid form. The applicator is illustrated in Figure 7. The apparatus consists of a cylindrical chamber which contains the adhesive components. The components are separated by a piston which is composed of two discs with matching holes. One of the two discs is free to rotate 30 degrees, thus isolating the adhesive components on each side of the piston. The second disc is fixed by a keyway in the side of the cylinder. The closure on the bottom end of the cylinder contains a 1/4" diameter orifice through which the adhesive is expelled. The orifice is closed by a side moving flap valve. The top end of the cylinder is closed by a plate with a central bearing for the shaft that controls the piston.



The activated adhesive is channeled into a tube after passing the rollers

Figure 5.

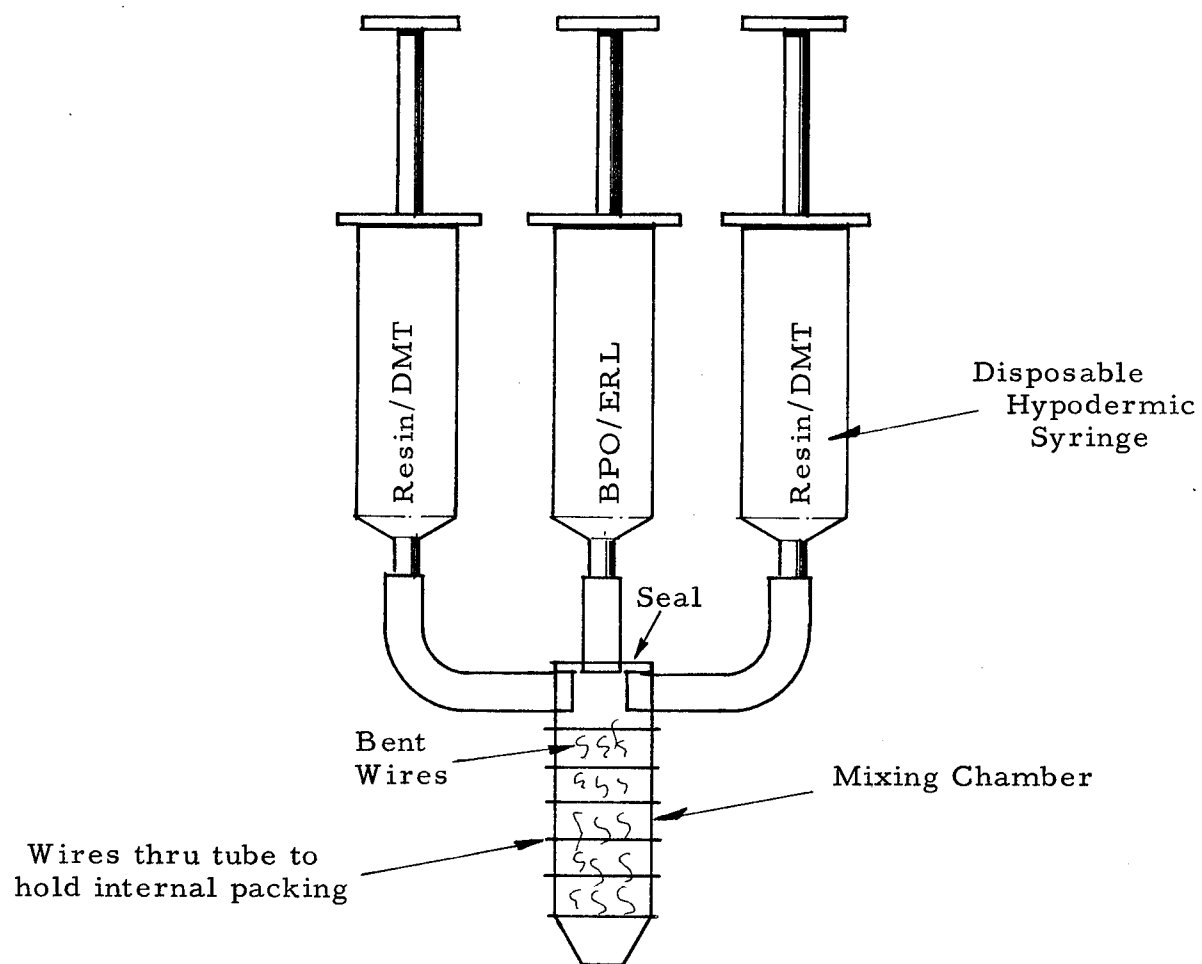


Figure 6. Mechanical Mixer

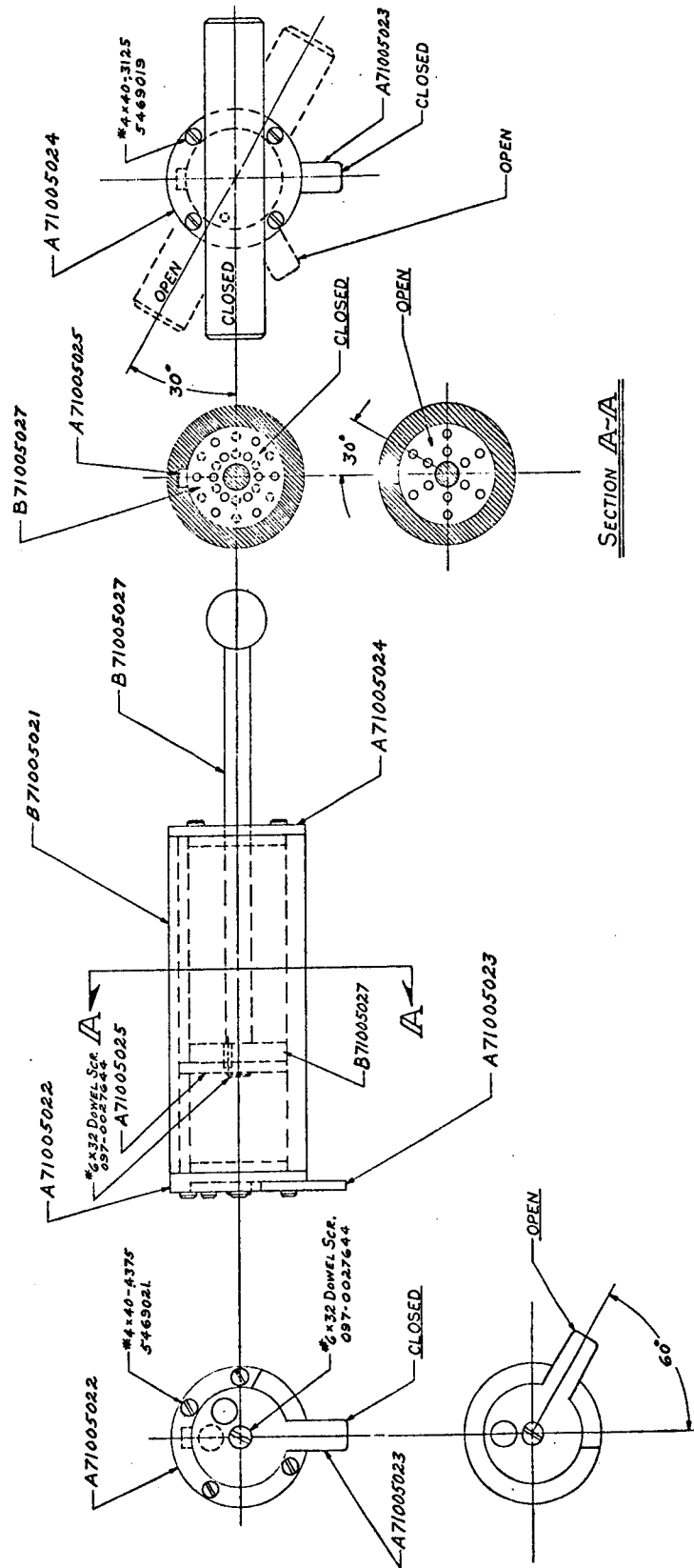


Figure 7. Mechanical Adhesive Applicator

The applicator is filled with the adhesive components by removing the four screws that secure the top plate to the cylinder. The top plate, handle, shaft and piston are removed. With the exit valve closed in the bottom of the cylinder, 25 ml of BPO/ERL solution is added to the cylinder. The piston should be checked to be sure the handle is turned so that the holes through the piston are in the closed position. The holes are opened and closed by rotating the handle 30 degrees counterclockwise when looking down on the handle. There is a detent in the piston for proper positioning. The piston is inserted into the cylinder until it is against the top of the adhesive component that has previously been added. The top plate is pulled up the shaft so that it is against the handle and the second adhesive component can be added above the piston. 50 ml of the polyester resin/DMT component is used. The top plate for the cylinder is secured in place by four screws.

To use the applicator for dispensing the adhesive, the handle is rotated 30 degrees clockwise, to open the ports in the piston. The handle is depressed to drive the piston to the bottom of the cylinder. The handle is then pulled to the top of the cylinder to mix the adhesive components. The handle is rotated 30 degrees in a counterclockwise direction to close the ports. The valve on the bottom of the apparatus is opened and the adhesive is expelled from the cylinder by depressing the handle to the bottom. One stroke of the handle gives a good mix, but if the adhesive formulation does not react too rapidly several strokes give a much better mix.

In the initial experiments with the adhesive applicator the percentage of peroxide in the epoxy resin was reduced from 20 to 15, because of the large mass of adhesive. The large mass of adhesive will cure very rapidly because of the high total exotherm. When 15% BPO/ERL 4221 was mixed with Aropol 7240MC containing 5% dimethyl p-toluidine, the adhesive cured in about 20 seconds from the time that it was first mixed. The formulation cures so rapidly that there was hardly time to eject it from the applicator.

In subsequent experiments (Table X) the peroxide concentration was reduced to 10 percent. There was very little difference in the cure rate between the 10 and 15% peroxide. The total mass of adhesive was too hot to touch. There are a few streaks of BPO/ERL that are slow to cure. There is a fair size area above the exit valve where a small quantity of material does not get mixed. There may also be a layer of material on the bottom of the chamber that does not receive adequate mixing. In the fast cure formulations where only one stroke of the piston is used there are usually several areas where the mix is poor. The operator of the dispenser is usually in a hurry to get the material mixed and out of the dispenser, and may not push the piston all the way down.

Table X - Formulations Tested in Mechanical Adhesive Applicator

<u>Formulation (position in mixing chamber)</u>	<u>Piston Strokes</u>	<u>Cure Time</u>	<u>Remarks</u>
5% DMT/Aropol (on top) 15% BPO/ERL 4221	one	20 sec	
5% DMT/Aropol (on top) 10% BPO/ERL 4221	one	20 sec	
5% DMT/Aropol (on top) 5% BPO/5% Azo-nitrile/ERL	one	20-30 sec	
5% DMT/10% TiO ₂ /Aropol 10% BPO/ERL 4221 (on bottom)	one	20-30 sec	
5% DMT/10% Vinyl/Aropol 10% BPO/ERL 4221 (on bottom)	one	30 sec	
5% DEA/Aropol (on top) 10% BPO/ERL 4221	one	2+ min	Oily film of DEA on surface
5% DEA/Aropol (on top) 10% BPO/ERL 4221	two	2 min	Oily film of DEA on surface
5% DEA/10% TiO ₂ /Aropol 10% BPO/ERL 4221 (on bottom)	two	2 min	Oily film of DEA on surface
5% DMT/2% RG 244/Aropol 10% BPO/ERL (on bottom)	one	30 sec	Poor mix Aropol comp. too thick
5% DEA/Aropol (on top) 5% BPO/5% Azo-nitrile/ERL	two	2 min	Oily film of DEA on surface
1% DMT/20% TiO ₂ /10% Vinyl VYLF/Aropol (on top) 5% BPO/5% Azo-nitrile/ERL	one	1-1/2-2 min	Poor mix
1% DMT/20% TiO ₂ /10% Vinyl VYLF/Aropol (on top) 5% BPO/5% Azo-nitrile/ERL	two	2 min	
2% DMT/20% TiO ₂ /10% Vinyl VYLF/Aropol (on top) 10% BPO/ERL	two	2 min	
2% DMT/20% TiO ₂ /Aropol 10% BPO/ERL	two	30 sec	
5% BPO/5% Azo-nitrile/ERL 2% DMT/20% TiO ₂ /Aropol	two	45 sec	Excellent mix
10% BPO/ERL 4221 (on top) 2% DMT/20% TiO ₂ /Aropol	two	30-40 sec	

Since there were a few streaks of the adhesive components that were slow to cure, 5 percent of the benzoyl peroxide was replaced by 5 percent 2, 2' azobis (2-methyl propionitrile) to determine if there was sufficient exotherm from the peroxide reaction to initiate a cure with the azo-nitrile compound and to give better cure propagation.

When the 5% azo-nitrile -5% BPO/ERL component was reacted with 5% DMT/Aropol the cure time was about 20 seconds. By visual evaluation, the cure of the adhesive mass appeared to be more uniform.

Since the reduction of the peroxide percentage did not extend the cure time, it was necessary to do something with the amine accelerator. Diethylaniline (DEA) was substituted for the dimethyl p-toluidine. In the first test made with the 5% DEA/Aropol the cure time was over two minutes. With the long cure time of the DEA, it was possible to increase the mixing time in the dispenser from one to two or three strokes. The additional mixing time in the apparatus shortened the cure time to less than two minutes.

When the diethylaniline is substituted for the dimethyl p-toluidine there is a slick film of diethylaniline on the surface of the adhesive. Because of the film of DEA, a reduced percentage of DMT was investigated. However the reduced percentage of DMT did not reduce the cure rate a great deal, but the addition of various fillers have had some effect.

In further tests the two adhesive components were reversed in the chamber to improve mixing and to have the void in the bottom of the chamber, above the exit vale filled with polyester resin component. By reversing the components there were fewer areas of slow curing adhesive because the cure propagation is best in the polyester resin.

There is a need for additional formulation work on the adhesive components to obtain a one minute cure. This can probably be accomplished best by reducing the filler level in the polyester resin component.

E. Batch Scale-Up

Scale up of the encapsulation procedures of both the epoxy and polyester resins progressed from the laboratory preparation of 2 liter batch to 7 liter lab batches and finally 30 gallon pilot plant batches. Some difficulty was encountered with the 7 liter batches, in the regulation of the agitation rate in order to obtain the desired emulsification and capsule size distribution. However further encapsulation studies proved successful and 30 gallon pilot plant batches were then prepared.

A total of 8 pilot plant batches were completed. Five of these batches used polyester and three epoxy resin as the encapsulant. Capsule yield percentages were improved as encapsulation and drying parameters were established. More studies may still be needed to insure capsule size reproducibility for the epoxy resin component.

1. Polyester Capsules

Five 30 gallon batches of the polyester resin component (5% DMT/5% TiO₂/Aropol 7240MC) were prepared in the pilot plant. The total capsule yields per batch were, 80.1%, 73.8%, 81%, 81% and 82.5%. A total yield of 60-62% was obtained in the desired size range of 840-1410.

The 68-70 pounds of polyester capsules obtained in the last two scale-up batches, were separated on a Sutton Steel air classifier due to difficulties encountered during screening of capsules of previous scale-up batches. Mechanical sieving of the capsules through standard screens results in the development of a static charge on the capsule walls. The statified capsules adhere to the screen and with further screening on a large scale capsule rupture is likely to occur.

Air classification alleviates the capsule rupture problem. The dried capsules are poured onto a vibrating, air fluidized bed which induces the larger capsules to migrate to the upper portion of the bed and the smaller capsules to the lower portion where each portion is separately collected. The apparatus was adjusted to yield three approximate size ranges; 300-500 μ , 500-800 μ , and 800-1400 μ . A distribution of 55% was obtained in the approximate size range of 800-1400 μ ; 40% in 500-800 μ ; and 5% in the 300-500 μ range.

About a pound of each classified cut was then hand sieved to obtain a distribution within that cut (Figure 8).

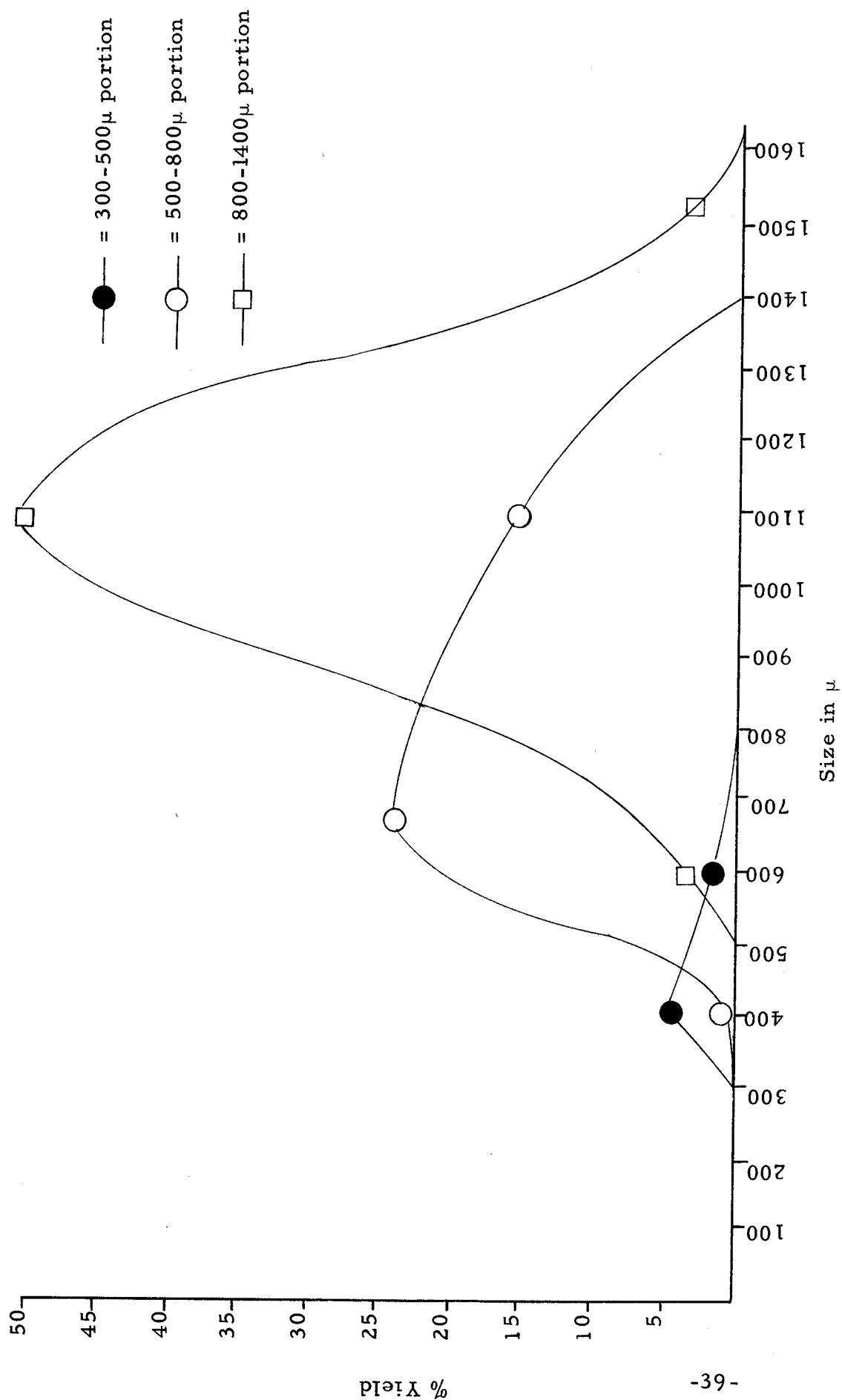
A large percentage of overlap of capsules within each size range was obtained. However, with additional work on the emulsification of the core material during encapsulation, the size range can be better controlled.

2. Epoxy Capsules

Three 30 gallon batches of 12% BPO/ERL 4221 capsules were prepared in the pilot plant. The first two batches gave rather poor yields of 74%. This was due to difficulties encountered during drying. With establishment of drying parameters (from Epoxy capsule drying procedure variation section) the third scale-up batch had an improved yield of 81%.

The first two batches had about a 50% yield in the desired size range of 800-1400 μ , while the third batch produced a smaller capsule size.

Figure 8. DMT/Polyester Capsule Size Distribution



A size distribution of 80% in the 500-800 μ range was obtained with 15% larger than 800 μ and 5% smaller than 500 μ . The capsules were hand sieved (about 25 lbs) since a charge of 50 pounds of capsules is needed to effectively operate the air classifier.

In order to increase pilot plant capsule size reproducibility and also increase the amount of final product per volume of encapsulation media (percent solids), the encapsulation procedure for BPO/ERL 4221 was modified in the laboratory. The amount of dilution water was decreased, thereby increasing viscosity of the encapsulation media. The increased viscosity aids in emulsification of the BPO/ERL 4221 mixture into the larger droplets. With a decrease in water, the pH of the encapsulated media was lowered, and excellent capsules were produced.

The decrease in dilution water also increases production efficiency because more capsules are obtained per volume of encapsulation media.

SECTION III CONCLUSIONS

Stability - Capsular stability of the DMT/polyester capsules was determined to be greater than 22 months (stability still being monitored). The stability of the BPO/epoxy capsules was limited to nine months in laboratory conditions. Total capsular adhesive stability is therefore limited to 9 months under ambient conditions.

Factors Affecting Stability - DMT/polyester capsules are not affected by light; however, slower reacting adhesive formulations containing DEA accelerated polyester capsules are susceptible to light. To ensure capsular stability from light, all adhesive formulations, whether DEA or DMT accelerated, should be stored in amber containers, or containers that protect the capsules from sunlight.

BPO/epoxy capsular stability is reduced when high temperatures are encountered during preparation, encapsulation and drying of the BPO/epoxy component. The 20% BPO/ERL 4221 capsules are the ones most affected by high temperatures.

The total capsular adhesive system is deactivated in high humidity due to DMT permeation of capsule walls. The total capsular adhesive must be stored in dry containers and when used in high humidity environments, must be activated within a short period of time in order to obtain maximum reactivity and bond strength.

Formulation Adjustments - The polyester/epoxy adhesive system is very versatile. Many formulation adjustments can be made depending upon ultimate adhesive requirements. Due to BPO crystal growth and resultant capsule wall rupture of BPO/epoxy capsules containing 12% BPO or greater, capsular adhesive formulations containing the 12% BPO/ERL capsules have greater stability which ensures adhesive reactivity reproducibility. Due to growth of BPO crystals and resultant wall rupture of capsule containing solutions greater than 12% BPO, greater stability is observed with formulations containing capsules of 12% or less BPO in ERL 4221.

Various thixotropic agents and resin flexibilizers can be formulated into the adhesive system which results in higher initial bond strengths.

However, lower ultimate bond strengths are realized when using these additives.

Scale-Up - Polyester and epoxy encapsulation procedures can be scaled-up from laboratory scale to 30 gallon pilot plant batches, as demonstrated by the successful preparation of five polyester and three epoxy capsule batches.

Mechanical Applicator - A variety of adhesive dispenser concepts were designed. One liquid-liquid mechanical applicator was fabricated and tested using fast and slow adhesive formulation. The fast adhesive system could not be used due to the inability of the applicator to properly mix and dispense the adhesive before it set. The slower reacting adhesive formulation could not be properly mixed thereby yielding a poor adhesive film.

Adhesion to Various Substrates - Adhesion and bond strengths of the adhesive formulations vary depending on the surface properties of the intended substrate. Bond strengths to dry, cold rolled steel are high while adhesion to submerged steel substrate is slightly reduced. Adhesion to various paint substrates is poor because of adhesive failure of the paint to the substrate. Very poor adhesion was encountered when bonding to submerged cold rolled steel. Bond strengths are greatly improved when the steel substrate is "pre-wetted" with a polyester/epoxy paste before activation of a slower reacting adhesive formulation. The resultant bond strength then meets contract requirements.

SECTION IV
RECOMMENDATIONS

1. Studies should continue toward the development of a highly practical and workable mechanical applicator for the dispensing of the total capsular adhesive system.
2. Studies should be initiated in order to develop an effective binder and coating system for the total capsular adhesive system.
3. Scale-up studies should be continued toward ultimate production quantities with emphasis on determination of handling and storage parameters for large volumes of capsules of sizes greater than 800 μ .
4. The capsular adhesive's adhesion properties to steel boiler plate, other metals, plastic and treated substrates should be investigated further in order to improve bond strengths.

APPENDIX

- A - List of Adhesive Ingredients
- B - List of Adhesive Formulations
- C - Encapsulation Processes
- D - Engineering Flow Diagrams
 - Polyester Encapsulation Process
 - Epoxy Encapsulation

APPENDIX A

List of Polyester / Epoxy Adhesive Ingredients

<u>Designation</u>	<u>Material</u>	<u>Supplier or Manufacturer</u>
Aropol 7240MC	- Polyester Resin	Ashland Chemical
ERL 4221	- Epoxy Resin	Union Carbide
DMT	- N,N Dimethyl p-toluidine	Aldrich Chemical
BPO	- Benzoyl Peroxide	Lucidol
TiO ₂	- Titanium Dioxide	MC & B
VYLF	- Polyvinyl Chloride - Polyvinyl Acetate Copolymer	Union Carbide
DEA	- Diethyl Aniline	Eastman Chemical
DPA	- N,N Dipropyl Aniline	Eastman Chemical

APPENDIX B

List of Polyester/Epoxy Adhesive Formulations

<u>Formulations</u>	<u>Parts by Weight</u>
<u>CA-13K (1-12)</u>	
Encapsulated 1% DMT/5% TiO ₂ /94% Aropol 7240MC	2
Encapsulated 12% BPO/ERL 4221	1
<u>CA-13K (2-12)</u>	
Encapsulated 2% DMT/5% TiO ₂ /93% Aropol 7240MC	2
Encapsulated 12% BPO/ERL 4221	1
<u>CA-13K (2-20)</u>	
Encapsulated 2% DMT/5% TiO ₂ /93% Aropol 7240MC	2
Encapsulated 20% BPO/ERL 4221	1
<u>CA-13K (5-12)</u>	
Encapsulated 5% DMT/5% TiO ₂ /90% Aropol 7240MC	2
Encapsulated 12% BPO/ERL 4221	1
<u>CA-13K (5-20)</u>	
Encapsulated 5% DMT/5% TiO ₂ /90% Aropol 7240MC	2
Encapsulated 20% BPO/ERL 4221	1
<u>CA-13K (5-20)V</u>	
Encapsulated 5% DMT/5% TiO ₂ /10% VYLF/80% Aropol 7240MC	2
Encapsulated 20% BPO/ERL 4221	1
<u>CA-13L (01-12)</u>	
Encapsulated 0.1% DEA/5% TiO ₂ /94.9% Aropol 7240MC	2
Encapsulated 12% BPO/ERL 4221	1
<u>CA-13M (01-12)</u>	
Encapsulated 0.1% DPA/5% TiO ₂ /94.9% Aropol 7240MC	2
Encapsulated 12% BPO/ERL 4221	1
<u>CA-15A</u>	
5% DMT/95% Aropol 7240MC	2
TiO ₂	2
Encapsulated 20% BPO/ERL 4221	1
<u>CA-15U (5-20)</u>	
5% DMT/95% Aropol 7240MC	4
VYLF	1
TiO ₂	1
Encapsulated 20% BPO/ERL 4221	2
<u>CA-18A</u>	
5% DMT/2% Asbestos RG-244/20% TiO ₂ /78% Aropol 7240MC	2
Encapsulated 20% BPO/ERL 4221	1

APPENDIX C

ENCAPSULATION PROCESSES

Coacervation Encapsulation System

In the coacervation process, the main components are gelatin, gum arabic and water. In the dilute solution region, coacervation can be attained by dilution, pH adjustment and temperature lowering. Under these conditions of low concentration, the gelatin acts as a positive colloid and the gum arabic as a negative colloid. The separating phase is a complex of both colloids. By pH adjustment, the gelatin becomes a positive colloid, that is, the amino groups are ionized to the NH_3^+ group, while at the same time, the gum arabic is negative due to the carboxy groups present. These oppositely charged macromolecules are attached to each other, thus neutralizing the excess charge and, as a result, the water solubility of this complex is reduced causing it to separate as a liquid phase.

In order to attain encapsulation, the material being encapsulated should be emulsified or dispersed in the colloid solution prior to obtaining the gelled coacervation conditions. The emulsified or dispersed material, which can be a liquid or a solid, acts as a seeding nuclei, about which the colloid rich phase is deposited as a continuous liquid phase.

Hardening of the capsule wall can be accomplished by crosslinking with various agents.

Non Aqueous Phase Separation

The approach to the encapsulation of water-soluble solids was by the phase separation technique. This technique employs preformed polymers and resins that are solvent soluble. From the number of preformed polymers and resins that have been examined, the phase separation principle appears to be generally applicable.

It has been demonstrated that this phase separation phenomenon can be employed successfully in the encapsulation of solids and liquids. It can be shown that when the clear solutions of two incompatible polymers dissolved in a common solvent are mixed, a turbid mixture results. Microscopic observation indicates the presence of a second liquid phase in the form of small droplets.

Unlike in situ polymerization techniques that are sensitive to contamination and difficult to control, this approach offers the ability to incorporate a wide latitude of properties into a polymer for achieving wettability, suitable cross-linking sites, and permeability control. Good control of the encapsulant can also be achieved by this phase separation technique.

To determine more completely the necessary conditions for encapsulation of water-soluble salts, two polymers were selected for an early study of phase separation. These were ethylcellulose and nitrocellulose. These polymers were readily phase separated out of solution by a polybutadiene polymer. It was found that for effective encapsulation, the viscosity of the separating phase controlled to a large extent the amount of wall deposited. The rate at which the viscosity increased, as the polybutadiene polymer was added, also controlled the size of the capsule formed, or the degree of aggregation. The wettability of the polymer phase was highly dependent on the solvent used and the functional groups present in the polymer. Finally, the concentration of the components governed, to a large number of commercially available polymers as wall materials.

Once the capsules are formed by this technique, they can be isolated from the solvent vehicle by several methods. These are crosslinking of the polymer, chelation with metallic ions, or by a non-solvent gelation. The capsules are then washed in a non-solvent and allowed to dry.

Melttable Dispersion

The melttable dispersion technique can be described as a process in which the wall material is deposited while in its molten state. The system requires the external phase to be a non-solvent to both the internal phase and the wall material. The dispersant liquids studied to date are silicones and fluorocarbons, which are relatively inert. The wall material is first dispersed in the dispersant liquid with agitation, followed by heating the system to the temperature at which the wall material is in a flowable state. The internal phase is now introduced and the system is slowly cooled, allowing the wall material to gradually solidify to form solid capsules. These capsules are then filtered and washed with a non-solvent. A product of free-flowing capsules is obtained.

The wall materials that have been employed with this technique are waxes, low-melting polyethylenes, as well as solid fats. Thus, a temperature release can be readily attained by this technique. The temperature range that has been achieved is 50 to 150°C.

The parameters that control the release characteristics and external phase to be established. The capsules are then filtered and resuspended in a fresh anhydrous solvent external phase which dehydrates the capsule wall. The solvent is filtered off and the capsules are air dried resulting in hard, brittle and glassy walled capsules.

Interfacial Polymerization Encapsulation by Polycondensation

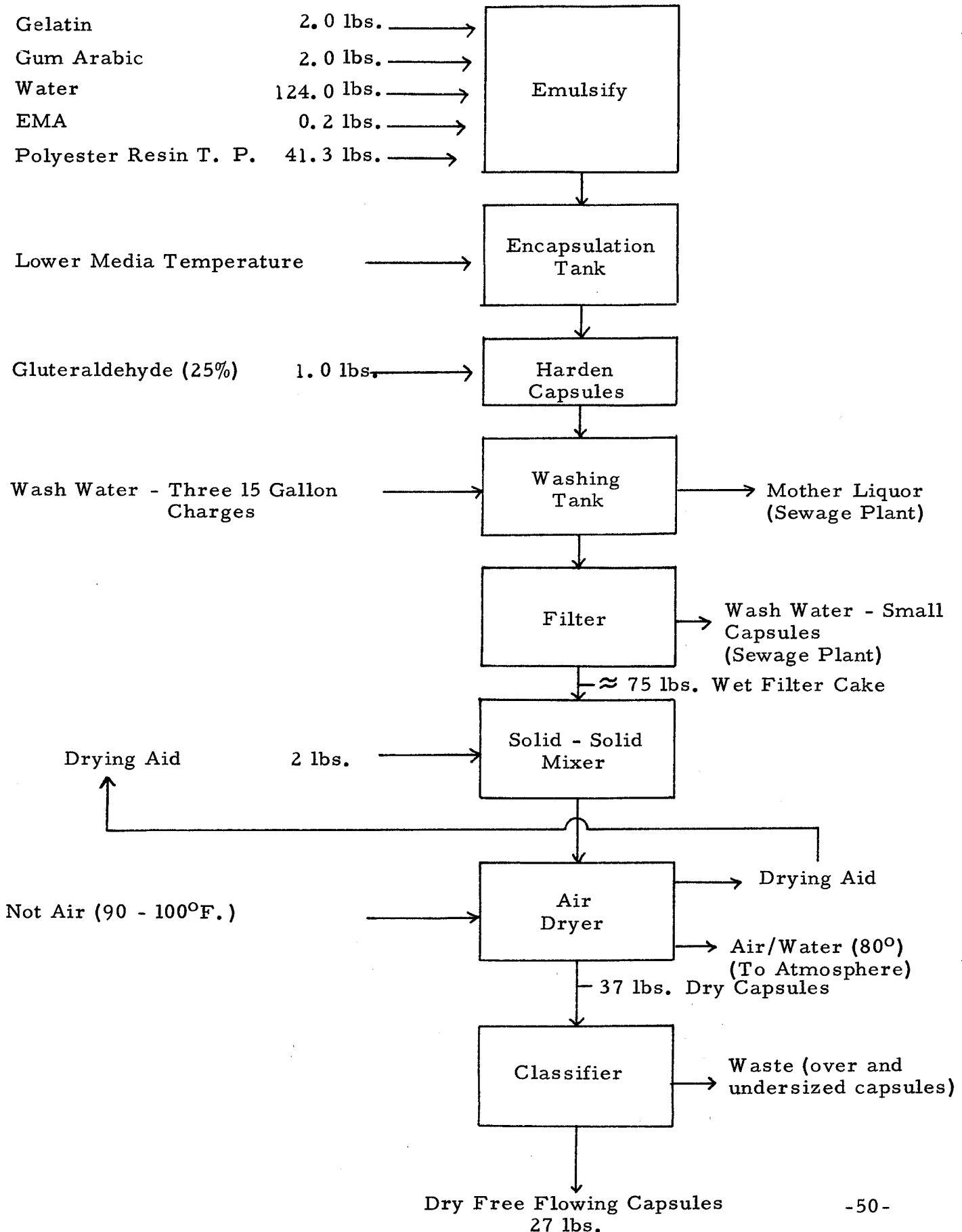
Interfacial polycondensation encapsulation is achieved by allowing a controlled reaction to take place between a reactive internal phase material and a second reactive compound dissolved in the matrix phase. The product of this reaction is a highly cross-linked polymeric material, as

evidenced by solubility studies. This polymerization formed polymer deposits as a protective wall around the remaining reactive internal phase material, thus encapsulating it.

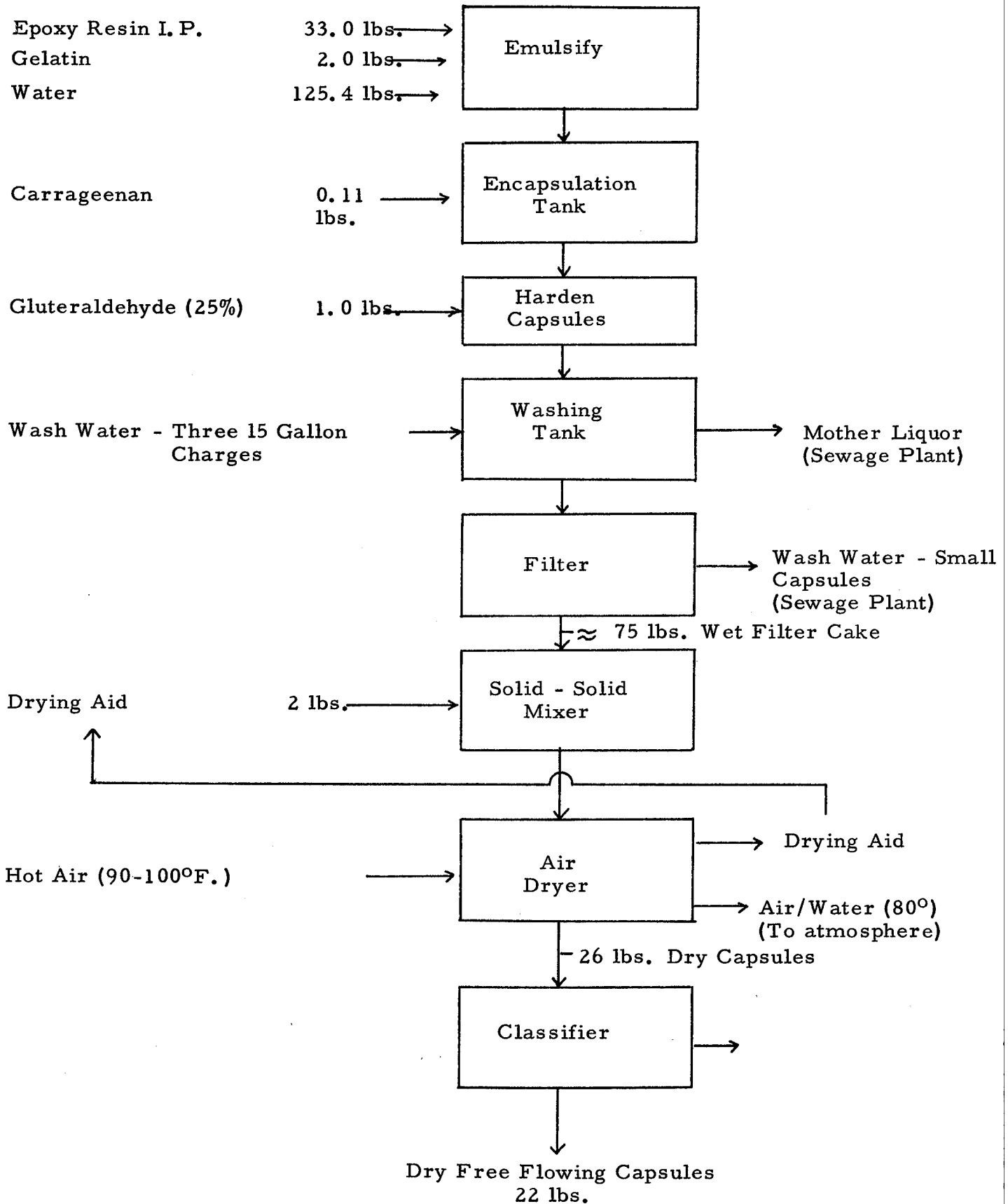
The capsules are recovered by removing the matrix liquid phase and washing the capsules with a suitable solvent. Air drying is utilized to complete the encapsulation process.

APPENDIX D

Polyester Encapsulation Process



Epoxy Encapsulation Process



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13. ABSTRACT During the initial phase of this program a unique, polyester-epoxy adhesive system was developed which cures very rapidly upon mixing of its two components and adheres to a multitude of substrates under various environmental conditions. Each of the two liquid adhesive components can be encapsulated to form "pseudo solids". Mixing together of the two capsular components into the proper ratio forms a stable, "one can," dry powder adhesive that is easily activated upon rupture of the capsules. This rapid curing capsular adhesive system, with its improved stability, handling and logistics characteristics due to encapsulation, was further characterized during the second phase of the program. Capsular adhesive stability was found to be nine months under laboratory conditions with the epoxy component being the limiting factor. Several formulation variations were made that affected cure time, bond strength and adhesion properties. Encapsulation of each of the two components was easily scaled up through the pilot-plant stage. Several mechanical adhesive applicator designs were developed and evaluated for the extrusion and application of both the capsular adhesives and the same formulations in their liquid, unencapsulated forms.			

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October 8, 1971

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Attention: Chief, Mr. H. Pebly

Gentlemen:

Enclosed herewith is the final report, Contract
DAAA-21-68-C-0581, entitled, "Development of Multi-
purpose Capsular Systems."

Sincerely,

A handwritten signature in cursive script that reads "John F. Hanny/so".

John F. Hanny, Assist. Manager
Research, Development
and Technical Services and
Military Marketing Manager
Capsular Products Division

JFH:so

Enclosure